

NEW CHEMICAL STRUCTURAL FEATURES OF COAL. STRUCTURE OF COAL DERIVATIVES (1)

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INTRODUCTION

The transalkylation reaction has been used by several researchers to investigate the structure of coal and other fossil fuels. Heredy and Neuworth (2) first applied the method to depolymerize coal under conditions that were mild enough so that unaltered monomeric units could be recovered. Their procedure consisted of heating coal with boron trifluoride in phenol. The boron trifluoride catalyst served to cleave aromatic-aliphatic bonds and phenol served as solvent and acceptor to give alkylphenols. The product fraction containing the alkylphenols was recovered and analyzed (3,4). This fraction was found to contain iso-propylphenol, ethylphenol and dihydroxydiphenylmethanes, thus confirming the presence of iso-propyl, ethyl, and methylene groups in coal. Further work was done with the coal-BF₃-phenol system by Ouchi (5) and Larsen (6). Later Franz (7) showed that certain phenolic derivatives undergo condensation reactions to give heterocyclic compounds which are not directly derived from coal.

The transalkylation reaction was further developed by Farcasiu (8), who used trifluoromethanesulfonic acid, CF₃SO₃H, as catalyst and xylene as solvent and acceptor. The method was useful in obtaining qualitative and quantitative information on methylene connecting groups and alkyl substituents in petroleum resids. We have modified this method for use in probing the structure of coal. Our method employs CF₃SO₃H as catalyst and toluene as solvent and acceptor (9). Using our version of the transalkylation reaction, we identified a large number of groups in coal (9) and compared the structures of nine different coals (10). Relevant model compound experiments were also reported. In this paper, we present preliminary information on the structure of the following products derived from coal: Pyridine extract and pyridine insoluble residue from Ky #9 coal, O-methylated Ill #6 coal, Birch reduced Ill #6 coal, Coke from Ill #6 coal, and SRC from Ky #9 coal.

EXPERIMENTAL

The procedure used here is the same as that used earlier (9,10). Briefly, 4 g of starting material are mixed with 20 ml of toluene after which 2 ml of CF₃SO₃H are added. The mixture is stirred under reflux for 48 hrs and then the reaction is quenched by adding NaHCO₃ and H₂O. An integration reference is added and the toluene solution is isolated and analyzed by capillary gc and capillary gc-ms. The original procedure calls for four consecutive reaction steps, or cycles, to recover most of the excisable groups. Here we report only selected data from the first reaction cycle. The data are recorded in Tables 1 and 2.

Coke was prepared by heating powdered Ill #6 coal in a quartz tube to 800°C for 1 hour in a stream of argon. O-Methylated coal was prepared by an adaptation of the Liotta procedure (11). Birch reduced coal was prepared by an adaptation of the Hombach procedure (12).

The material referred to as SRC is filtered SRC T102 bottoms, Run No. 72, K125, Date-4/19/76, SN No. 74690, supplied by W. H. Webber, EPRI.

RESULTS AND DISCUSSION

The mechanism (13) for transfer of ethyl groups, or other n-alkyl groups, from benzene to toluene is shown in Figure 1. Extension of the mechanism suggests that 1,1-ditolyethane also should appear in the product mixture. Assuming that the benzene ring is replaced by a coal aromatic cluster and ethyl is any n-alkyl group, it is anticipated that n-alkyltoluenes, 1,1-ditolyalkanes and a variety of free

aromatics will appear in the product mixture. Tertiary alkyl groups transfer through free cationic intermediates while secondary alkyl and benzylic groups probably transfer through mixed mechanisms.

Actually, a large number of derivatives of toluene as well as other compounds are found in the product mixture (9,10). For the present discussion we have selected a limited number of these compounds. The selection is made on the basis of two criteria: these groups are the most prevalent in most of the samples, and they represent groups which demonstrate similarities or differences between the samples. Other important aspects of the results will be presented in a future paper along with 2nd-4th cycle results.

Table 1 contains data obtained from the transalkylation of Ill #6 coal and its derivatives, while the data for Ky #9 coal and its derivatives are collected in Table 2.

From Table 1 it is seen that O-methylation of Ill #6 coal causes only small changes in the numbers of excisable groups. Only ethyl and propyl are significantly lower in value. From these results, we suggest that O-methylation of coal by the Liotta procedure (12) produces only minor structural changes.

Results from the transalkylation of Birch reduced coal are found in Table 1, column 4. These results also show reduced amounts of certain monosubstituted alkyl groups, while the amounts of 1,1-diarylkalkanes are larger. The increased values of 1,2-ditolylethane can be a consequence of reaction of triglyme, used as solvent in the Birch reduction, which may not have been completely removed by washing and drying the coal. The methine cross linking group, represented by tritolylmethane, has been lowered in concentration relative to the parent coal, while the trisubstituted ethane has been increased. The observation relative to trisubstituted ethane will be resolved in future control experiments. Another observation not shown in the Tables is that changes in coal structure during Birch reduction resulted in the production of large numbers of substituted indane and tetralins during transalkylation.

The data on coke presents an interesting case. The coking process effectively drives off volatile matter and causes thermal cleavage of many bonds so that many substituent groups are removed. The remaining residue is thought to be a network of polynuclear aromatics with few excisable side chains. This expectation is borne out by the experimental data in Table 1. Only small amounts of ethyl and methylene substituents are found. The most abundant transalkylation product is an assembly of isomers of a compound which has a molecular weight of 214. This compound, not shown in the Tables, has not yet been identified.

The pyridine extract and pyridine insoluble residue from Ky #9 coal, Table 2 and Figure 2, show some large differences. The soluble part shows increased amounts of monosubstituted alkyl substituents, while the insoluble part is partially depleted in these groups. There is a decrease in the amount of 1,1-diarylethane in both fractions. The relationship between 1-substituted alkyls and 1,1-disubstituted alkyls can be explained by reference to the mechanistic scheme in Figure 1, and the proposed presence of larger numbers of hydride abstractors as set forth in the section on model systems.

The most dramatic change is seen in the differences in concentrations of ditolylmethane and tritolylmethane in the soluble and insoluble fractions. The soluble part contains the larger amount of ditolylmethane which represents methylene ($-\text{CH}_2-$) connecting groups between aromatic clusters. On the other hand, the insoluble part contains the larger amount of tritolylmethane which represents methine ($>\text{CH}-$) crosslinking groups. These data are in agreement with the accepted opinion that pyridine extracts the material with a lower cross-link density and leaves a residue with a higher cross-link density.

SRC contains smaller molecules and more soluble materials. It is about 90% soluble in toluene. It is observed to contain a larger number of alkyl substituents and, as expected, a lower number of methylene connecting groups relative to the starting coal.

We have performed numerous experiments with model compounds in order to better understand results with coal and coal products. The most significant aspects of

these experiments are summarized as follows: In an earlier paper (9), we showed that n-alkylbenzenes transalkylate slowly under our experimental conditions. In contrast, n-alkyl substituents on polynuclear aromatics, such as phenanthrene, anthracene and pyrene, transalkylate 10-100 times faster. We also found that alkyl substituted aromatics transalkylate 2-5 times faster when the reaction mixture contains polynuclear aromatics. The latter observations are probably a result of the much larger basicity of the polynuclear aromatics and the hydride abstracting ability of their protonated intermediates. Because transalkylation takes place through a chain mechanism, the presence of more hydride abstractors increases the rate by increasing the number of chain initiation steps. With these concepts in mind, it is reasonable that the polynuclear nature of coal accounts, at least in part, for the rapid production of numerous toluene derivatives under our reaction conditions.

CONCLUSIONS

The above discussion is based on preliminary data observed from coal derivatives. The data show certain trends, such as:

1. O-methylation does not appear to change the structure of coal greatly.
2. The treatment of coal under alkali metal reducing conditions appears to lower the number of excisable short chain alkyl substituents while also changing the structure to give new compounds under transalkylation conditions.
3. Pyridine extraction produces two fractions which have widely different substituent features.

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TABLE 1.

Results from the transalkylation of products derived from 111 #6 coal compared with the parent coal.^a

	Parent	-OCH ₃	Birch Red.	Coke
Ethyltoluene	0.47	0.30	0.17	0.029
Propyltoluene	0.25	0.19	0.089	0.0066
Butyltoluene	0.053	0.040	0.045	---
Pentyltoluene	0.008	0.014	0.010	---
Phenyltolylmethane	0.018	0.022	0.016	---
Ditolylmethane	1.09	1.14	0.55	0.036
1,1-Ditolylethane	0.098	0.014	0.21	0.0010
1,2-Ditolylethane	0.037	0.039	0.088	0.0018
1,1-Ditolylpropane	0.021	0.040	0.041	---
Tritolylmethane	0.025	0.028	0.011	0.0012
1,1,2-Tritolylethane	0.019	0.023	0.070	---
Naphthalene	0.009	0.0079	0.0025	---
Methyl naphthalene	0.045	0.040	0.011	---
Dimethylnaphthalene	0.034	0.034	0.016	---
Trimethylnaphthalene	0.014	0.011	tr	---
Methyltolyl naphthalene	0.014	0.029	tr	---

^aResults are in mmol per 4 g of starting coal.

TABLE 2.

Results from the transalkylation of products derived from Ky #9 coal compared with the parent coal.^a

	Parent	PySol	Insol	SRC
Ethyltoluene	0.30	0.41	0.058	0.50
Propyltoluene	0.16	0.21	0.056	0.19
Butyltoluene	0.041	0.12	0.028	0.063
Pentyltoluene	0.016	0.020	0.0047	0.037
Phenyltolylmethane	0.029	0.018	0.035	0.012
Ditolylmethane	1.11	0.988	0.614	0.59
1,1-Ditolylethane	0.19	0.11	0.019	0.027
1,2-Ditolylethane	0.025	0.036	0.0069	0.012
1,1-Ditolylpropane	0.060	0.054	0.042	0.014
Tritolylmethane	0.057	0.019	0.12	0.006
1,1,2-Tritolylethane	0.049	0.024	0.019	---
Naphthalene	---	0.012	0.0027	0.027
Methyl naphthalene	0.067	0.057	0.040	0.037
Dimethylnaphthalene	0.027	0.056	0.019	0.022
Trimethylnaphthalene	0.0092	0.028	0.0055	tr
Methyltolyl naphthalene	0.013	0.12	0.015	---

^aResults are in mmol per 4g of starting coal.

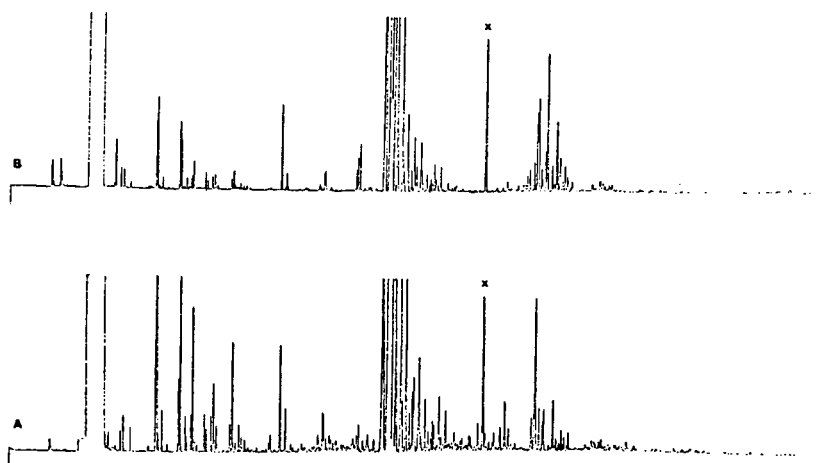


Figure 2. GC Traces of Transalkylation Products from A) Pyridine Soluble Fraction of Ky 99 Coal. B) Pyridine Insoluble Fraction. The Peak Marked X is Triphenylmethane Added as Internal Reference.

ORNL DMC 84-18170

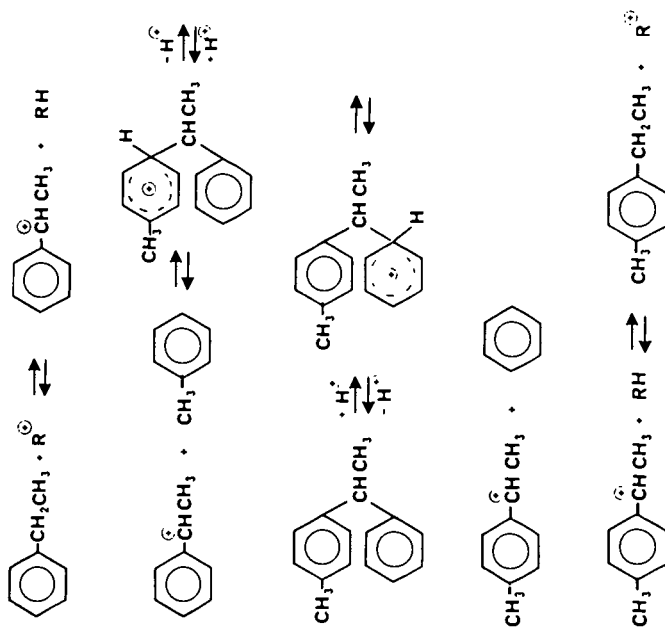


Figure 1. Mechanism of Transalkylation of Ethylbenzene in Toluene